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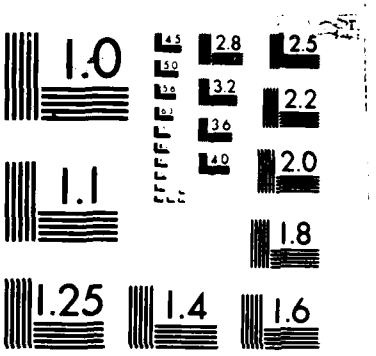

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USAFOEHL REPORT

87-002EH0410AAC

AIR SAMPLING OF POLYCHLORINATED DIBENZO-DIOXINS, POLYCHLORINATED DIBENZOFURANS, AND POLYCHLORINATED BIPHENYLS ARNOLD AFS TN

ISAAC ATKINS, JR., CAPTAIN, USAF, BSC

January 1987

FINAL REPORT

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USAF Occupational and Environmental Health Laboratory
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235-5501

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The 4960 ABS/SGPE, Arnold AFS TN requested USAFOEHL determine if office areas adjacent to the tunnel "F" polychlorinated biphenyl (PCB) fire of March 1984 exceeded occupational exposure levels for PCBs and its decomposition products. This report explains how USAFOEHL determined ambient levels of polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and PCBs at Arnold AFS. The PCDDs and PCDFs of interest included 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) as well as tetra through octa chlorinated congener classes of dioxins and furans.

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Contents

I. INTRODUCTION

A. Background

On 25 March 1984, a fire occurred in the basement of the Tunnel "F" building at Arnold AFS TN. Areas affected by the fire included the north end of the basement near the welding shop and alongside the north-south wall. An electrical wire caused an electrical short to melt its conduit container. The conduit container ignited a fiberglass insulated wood stud and a pallet of heavy wire used in Ling amplifier equipment. This equipment contained 24 polychlorinated biphenyl (PCB) capacitors. Apparently, PCB leaked from one of the capacitors and was consumed in the fire. Smoke and soot was distributed throughout the basement and in adjacent office areas by the ventilation system and fire fighting operations.[1]

Subsequent sampling and analysis of soot and swipe samples contained significant quantities of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in addition to PCBs.

The 4960 ABS/SGPE requested USAFOEHL determine if office areas adjacent to the March 1984 PCB fire exceeded occupational exposure levels for PCDDs, PCDFs and PCBs. This entailed the collection and analysis of air samples for PCDDs, PCDFs, and PCBs.

On 9 Jul 86 USAFOEHL collected five air samples plus a blank for PCDDs and PCDFs, and four air samples plus a blank for PCBs. The results indicated the office workers in the adjacent office areas to the March 1984 PCB fire were not occupationally exposed to hazardous levels of PCDDs, PCDFs or PCBs; however, the basement and tunnel "F" areas were above the recommended level of 10 picograms (pg) per cubic meter (m^3) of total 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) equivalents.

B. Objective of Current Report

The purpose of this report is to explain how USAFOEHL determined ambient levels of PCDDs, PCDFs, and PCBs at Arnold AFS. The PCDDs and PCDFs of interest included 2,3,7,8-TCDD and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) as well as the tetra through octa chlorinated congener classes of dioxins and furans.

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II. AIR SAMPLING AND ANALYSIS

A. PCB

NIOSH method 5503 was used to determine ambient concentrations of PCBs. This method consisted of a 13 mm glass fiber filter (without binders) housed in a Swinnex cassette. This device was followed by a 7 cm long, 6 mm outer diameter, 4 mm inner diameter glass tube containing two sections of 30/48 mesh deactivated florisil. The sampling rate was 1.5 liters per minute (LPM) over a 7 hour period. Refer to Table I for PCB sampling protocol. The limit of detection was 5 micrograms (µg) per sample. Samples were analyzed by USAFOEHL/SA using gas chromatography with radio-labeled Nickel (63) electron capture detection.[2]

B. PCDD and PCDF

Air samples for PCDFs and PCDDs were collected using a two-stage high volume air sampling device obtained from USAFOEHL (see Figure 1). The device is similar to a device developed by the New York State Department of Health and previously demonstrated in the Binghamton State Office Building PCB transformer fire. The sampling device has been used in the field to determine air concentrations of PCDFs and PCDDs in the range of 5-100 pg/m^3.

The sampling device consisted of two stages: a 47 mm glass microfiber (EPM 2000, 0.3 micrometer) collecting particulate filter, and a glass absorption cartridge containing glass wool and 8 grams of 140 degrees Celsius activated 30/40 mesh silica gel. The glass cartridge containing the silica gel adsorbent was housed in an aluminum housing and sealed with fluorelastomer viton "O" rings.

The PCB and PCDD/PCDF sampling trains are shown in Figure 2. The PCDD/PCDF samplers were connected with rubber tubing to a 1.5 cubic feet per minute Millipore vacuum pump. Rotameters were used to regulate the air flow rate. The air flow rate through the device ranged from 12 to 20 liters per minute. Refer to Table I for PCDD/PCDF sampling protocol. Prior to sampling, the samplers containing the silica gel absorption cartridges were placed in desicators and each spiked by Battelle Laboratory with 2.5 nanograms (ng) of the following isotopically labelled internal standards:

2,3,7,8-tetrachlorodibenzo-p-dioxin-$^{13}C_{12}$ (2,3,7,8-TetraCDD-$^{13}C_{12}$) and 2,3,7,8-tetrachlorodibenzofuran$^{13}C_{12}$ (2,3,7,8-TetraCDF-$^{13}C_{12}$).

The samplers containing the absorption cartridges were then returned to Arnold AFS for sampling. After sampling, the samplers containing the absorption cartridges were wrapped in aluminum foil and placed in desicators and sent to Battelle for analysis. The glass microfiber filter and absorption cartridges were analyzed using a Carlo Erba Model 4160 high resolution gas chromatograph which interfaced directly into a VG Model 7070-H high resolution mass spectrometer. The limit of detection was 1 pg/m^3 per sample per congener class.

III. EXPOSURE STANDARDS

A. General

The National Institute for Occupational Safety and Health (NIOSH) recommends "PCBs and TCDD be considered as potential human carcinogens in the workplace. Limited evidence from animal and human studies suggests PCDFs may also pose a risk to human health. As prudent public health policy, NIOSH recommends occupational exposure to PCBs, PCDFs, and PCDDs resulting from electrical equipment fires or failures be controlled to the lowest feasible limit."[3]

B. PCB

The Occupational Safety and Health Administration promulgated its permissible exposure limit (PEL) of 1 milligram per cubic meter (mg/m^3) of air for chlorodiphenyl products containing 42% chlorine and 0.5 mg/m^3 for chlorodiphenyl products containing 54% chlorine determined as an 8-hour time-weighted average (TWA). Concentrations were based on the 1968 Threshold Limit Values (TLVs) of the American Conference of Governmental Industrial Hygienists (ACGIH). The TLVs, which have remained unchanged at 1 mg/m^3 (42%) and 0.5 mg/m^3 (54%) through 1985, are based on the prevention of liver injury in exposed workers. The ACGIH Short Term Exposure Limits (STEL) for chlorodiphenyls are 2 mg/m^3 and 1 mg/m^3 for 42% and 54% chlorine products, respectively. The OSHA PEL and the ACGIH TLV and STEL values include a "Skin" notation which refers to the potential contribution to overall exposure by the cutaneous route, including the mucous membranes and eyes, by either airborne or direct skin contact with PCBs.[4]

C. PCDDs and PCDFs

Currently, no national accepted occupational exposure standards exist for dioxins or furans. Different reentry guidelines have been used by health departments in states where PCB transformer fires have occurred. The procedure used by the New York State Department of Health (NYSDOH) following the Binghamton fire has received the most attention in the literature and is the criteria USAFOEHL recommends.

For the Binghamton fire, the concept of a "2,3,7,8-TCDD equivalent" was utilized to estimate the toxicological potential of the soot that existed in the building. The 2,3,7,8-TCDD equivalent is an algorithm which includes the measured concentration of the most highly toxic PCDD and PCDF congeners.

The use of the algorithm permits an estimation of PCDF and PCDD concentrations by assigning weighting factors (numbers) to each significant isomer class based on its relative toxicity to 2,3,7,8-TCDD. Table II was used to compute the total 2,3,7,8-TCDD equivalent for this survey. Each toxicologically significant PCDF and PCDD isomer concentration (pg/m^3) was multiplied by its relative class toxicity factor and its chlorine substitution factor. The result was a "2,3,7,8-TCDD equivalent concentration". Then, each 2,3,7,8-TCDD equivalent concentration was summed to reach a "total sample 2,3,7,8-TCDD equivalent concentration." This procedure was reaccomplished for each sample. Table III summarizes the total 2,3,7,8-TCDD equivalent calculation for each sample.

The NYSDOH assembled an Expert Advisory panel, which consisted of government industrial hygienists and international scientists, to establish reentry guidelines for the Binghamton office building. The panel developed a combined air and surface guideline based on a maximum safe daily intake of 2 picograms per kilogram per day (pg/kg/day) of body weight of 2,3,7,8-TCDD equivalents for a lifetime exposure. This level of intake was derived by applying an uncertainty factor of 500 to a No-Observed-Effect Level (NOEL) of 1 ng/kg/day in a three generation study of rats. This risk assessment is based on a 50 kg person with a respiratory volume of 10 m^3 per 8-hour day.[5]

$$\frac{1 \times 10^{-9} g/kg/day \text{ (NOEL)}}{500 \text{ uncertainty factor}} = 2 \text{ pg/kg/day}$$

$$2 \text{ pg/kg/day} \times 50 \text{ kg person} = 100 \text{ pg/day}$$

$$100 \text{ pg/day} \times \frac{1 \text{ day}}{10 \text{ m}^3} = 10 \text{ pg/m}^3 \text{ of total 2,3,7,8-TCDD equivalents}$$

IV. RESULTS AND DISCUSSION

Five air samples plus a blank for PCDD and PCDF, and four air samples plus a blank for PCB were analyzed. These samples are listed in Table III. As shown in Table III, the PCB concentrations were reported to be less than 0.008 mg/m^3 (far less than the ACGIH 8-hour TLV, 1 mg/m^3). USAFOEHL/SA analyzed the PCB samples and Battelle Laboratory analyzed the PCDD and PCDF samples. Prior to sampling, the PCDD and PCDF samplers were spiked by Battelle Laboratory with isotopically labelled internal standards. The internal standards average recoveries ranged from 47% to 62%, as shown in Table IV. Table V summarizes the quantification of the PCDDs and PCDFs air samples in pg/m^3. All five actual air samples contained low levels of Octa-CDD, but no 2,3,7,8-TCDD was detected. Sample No. 1 contained detectable levels of Hepta-CDD. 2,3,7,8-TCDF was detected in all five air samples, with sample No. 2 being the highest (140 pg/m^3). The field control sample did not contain detectable levels of chlorinated dioxins or furans. In general, the levels of furans decreased as the level of chlorination increased.[6]

The sampling results indicated the office workers in the adjacent office areas to the March 1984 PCB fire were not occupationally exposed to hazardous

levels of PCDDs, PCDFs, or PCB; however, Table III showed the basement (17 pg/m^3) and the tunnel "F" (50 pg/m^3) areas exceeded the 10 pg/m^3 of total 2,3,7,8-TCDD equivalent criteria established by the NYSDOH and recommended by USAFOEHL. USAFOEHL recommends actions be taken to lower the PCDD and PCDF levels in both areas.

V. RECOMMENDATIONS

A. Provide adequate ventilation in the basement and tunnel "F" areas. The basement and tunnel "F" areas' ventilation system was inoperative when the samples were taken. This may have contributed to the high levels found in both of these areas.

B. Apply a sealant or coating to the basement and tunnel "F" areas to seal in the PCDD and PCDF particulates. This will trap the particulates within the coating and reduce the regeneration of particulates into the air. Cover as much surface area with sealant as possible.

C. Resample the basement and tunnel "F" areas after the sealant is applied and the ventilation system is operational. If the PCDD or PCDF air concentrations remain above 10 pg/m^3 of total 2,3,7,8-TCDD equivalents, base bioenvironmental engineering personnel should implement control measures (i.e., isolation of the high contaminated zones, limited work duration or personnel protective equipment) to limit occupational exposure to these chemicals.

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5. Kim, K. Nancy, Hawley, John. "Re-entry Guidelines Binghamton State Office Building." Bureau of Toxic Substance Assessment Division of Health Risk Control New York State Department of Health, Albany, New York 12237 (August 1984)

6. Battelle Laboratory Report. Determination of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Ambient Air Samples, (26 Sept 1986)

TABLE I

PCB SAMPLING Protocol

Sample No.	Location	Sampling Time (min)	Sample Flow-rate (LPM)	Total Volume Collected (liters)
1	Base/Tent side	420	1.5	630
2	1st Floor Tunnel "F"	420	1.5	630
3	1st Floor Dr Ritter Office	420	1.5	630
4	Old Machine Shop	420	1.5	630

Limit of Detection 5 micrograms per sample

PCDF and PCDD Sampling Protocol

Sample No.	Location	Sampling Time (min)	Sample Flow-rate (LPM)	Total Volume Collected (liters)
1	Basement/Test side	2460	20	49,200
2	1st Floor Tunnel "F"	2437	12	29,244
3	1st Floor Dr Ritter office	2418	14	33,852
4	Room 220 Computer Rm	2427	12	29,124
5	Old Machine Shop	2416	12	28,992

Limit of Detection 1 picograms per sample per congener class

Table II

CALCULATION OF 2,3,7,8 TCDD EQUIVALENTS

(see notes below)

Isomer or Group	Conc.		Relative Class Toxicity	X	Relative Toxicity of Chlorine Substitution	=	2,3,7,8 TCDD Equiv.
2,3,7,8 TCDD	C		1	X	1	=	_____
2,3,7,8 TCDF	C		1.333	X	1	=	_____
Total PentaCDD	C		1	X	0.15	=	_____
Total PentaCDF	C		0.333	X	0.15	=	_____
Total HexaCDD	C		1	X	0.06	=	_____
Total HexaCDF	C		0.333	X	0.05	=	_____
Total HeptaCDD	C		1	X	0.014	=	_____
Total HeptaCDF	C		0.333	X	0.014	=	_____
					Total 2,3,7,8 TCDD Equivalents	=	_____

Note a: Results may indicate the presence of isomers not listed in Table II. Only consider the toxicologic significant isomers that are listed in Table II for calculation of the total 2,3,7,8 TCDD equivalent.

Note b: To use Table II, locate the isomer group(s) identified from your sampling results in the Table. Only the isomers found in Table II should be considered for this computation. Multiply the isomer group(s) concentration C by the relative class toxicity factor and the chlorine substitution factor. The result is a "2,3,7,8 TCDD equivalent. Do the same for each PCDD and PCDF isomer found in your sample that is shown in Table II. Then, sum each 2,3,7,8 TCDD equivalent concentration to reach a "total 2,3,7,8 TCDD equivalent concentration".

TABLE III

SAMPLING RESULTS

Sample No.	Location	Total 2,3,7,8, TCDD equivalent (pg/m^3)	PCB Concentration
1	Basement/Test side	17*	ND
2	1st Floor Tunnel "F"	50*	ND
3	1st Floor Dr Ritter Office	1	ND
4	Room 220 Computer Room	3	
5	Old Machine Shop	2	ND

*This area exceeds the recommended criteria of 10 pg/m^3 total 2,3,7,8 TCDD equivalents.

ND--Non-detected. PCB concentration less than 0.008 mg/m^3 (far less than ACGIH 8-hour TLV, 1 mg/m^3).

TABLE IV

RECOVERY DATA FOR INTERNAL STANDARDS, %

SAMPLE NO.	2,3,7,8-TetraCDD $^{13}C_{12}$	2,3,7,8-TetraCDF $^{13}C_{12}$	PentaCDD $^{13}C_{12}$	PentaCDF $^{13}C_{12}$	HextaCDD $^{13}C_{12}$	HextaCDF $^{13}C_{12}$	OctaCDD $^{13}C_{12}$
FIELD CONTROL SAMPLE	73.4	61.3	59.7	67.8	47.0	45.5	35.7
5	60.5	60.5	61.8	69.8	48.6	46.0	38.1
4	61.2	69.3	63.7	68.7	49.4	49.5	41.0
1	66.2	68.4	70.2	79.8	51.3	52.0	45.6
2	55.6	53.5	56.1	61.7	37.3	40.4	27.9
3	60.0	59.3	62.6	70.7	50.1	50.0	42.3
NATIVE SPIKE	45.9	53.8	62.7	66.2	52.5	52.3	40.6
METHOD BLANK	48.7	54.2	53.1	58.4	41.5	42.1	32.8
$\bar{X}$	58.9	60.1	61.2	67.9	47.2	47.2	38.0
%RSD	15.1	11.2	8.4	9.4	11.1	9.4	15.0

Table V

QUANTIFICATION OF AIR SAMPLES, pg/m³

SAMPLE No.	CUBIC METER	2,3,7,8-TetraCDD	TetraCDD	PentaCDD	HexaCDD	HeptaCDD	OctaCDD
Field Control Sample	30	ND(0.48)	ND(0.48)	ND(0.45)	ND(0.42)	ND(1.07)	ND(6.0)
1	57	ND(0.27)	ND(0.27)	ND(0.45)	ND(0.14)	0.50	6.9
2	29	ND(0.76)	ND(0.76)	ND(0.42)	ND(0.51)	ND(1.49)	13.7
3	34	ND(0.31)	ND(0.31)	ND(0.31)	ND(0.41)	ND(0.99)	7.7
4	29	ND(0.54)	ND(0.54)	ND(0.30)	ND(0.34)	ND(1.71)	8.7
5	29	ND(0.45)	ND(0.45)	ND(0.44)	ND(0.32)	ND(1.08)	6.6
Native Blank	30@	230	230	170	170	150	130
Method Blank	30	ND(0.80)	ND(0.80)	ND(0.90)	ND(0.54)	ND(1.67)	3.1

SAMPLE No.	CUBIC METERS SAMPLED	2,3,7,8-TetraCDF	TetraCDF	PentaCDF	HexaCDF	HeptaCDF	OctaCDF
Field Control Sample	30	ND(0.72)	ND(0.72)	ND(0.21)	ND(0.42)	ND(0.80)	ND(1.16)
1	57	46.0	370	29.8	0.37	ND(0.47)	ND(0.48)
2	29	140	1200	59.0	1.20	ND(0.27)	ND(1.21)
3	34	3.2	29.0	1.03	ND(0.20)	ND(0.46)	ND(0.89)
4	29	8.2	73.9	3.7	ND(0.20)	ND(0.99)	ND(1.25)
5	29	5.8	51.0	2.0	ND(0.16)	ND(0.64)	ND(1.11)
Native	30@	210	210	160	170	160	120
Method	30	ND(0.53)	ND(0.53)	ND(0.35)	ND(0.27)	ND(0.97)	ND(1.99)

@ - For the native spike sample, 30 m³ was used for quantification. Each congener was spiked at 167 pg/m³.

ND - Non-detected (Limit of Detection).

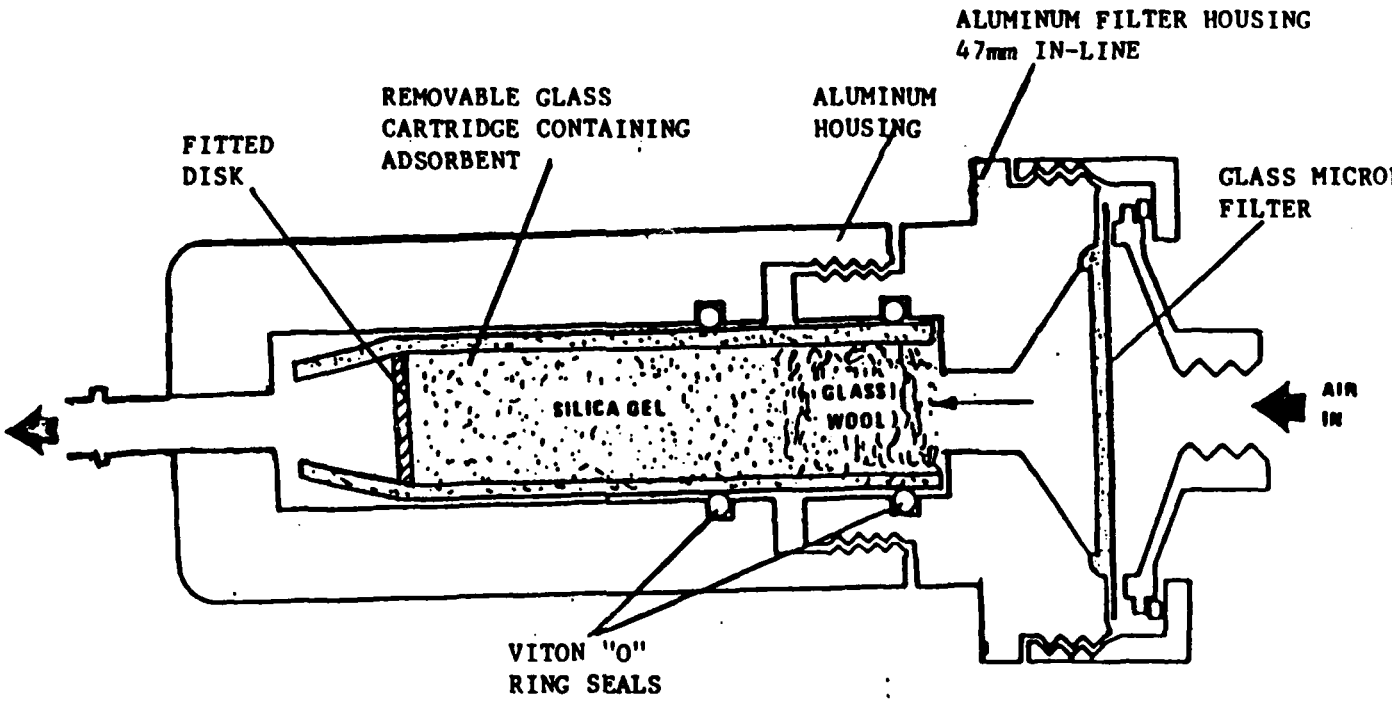

FIGURE 1. TWO STAGE AIR SAMPLING DEVICE FOR PCDFs/PCDDs DEVELOPED BY USAFOEHL

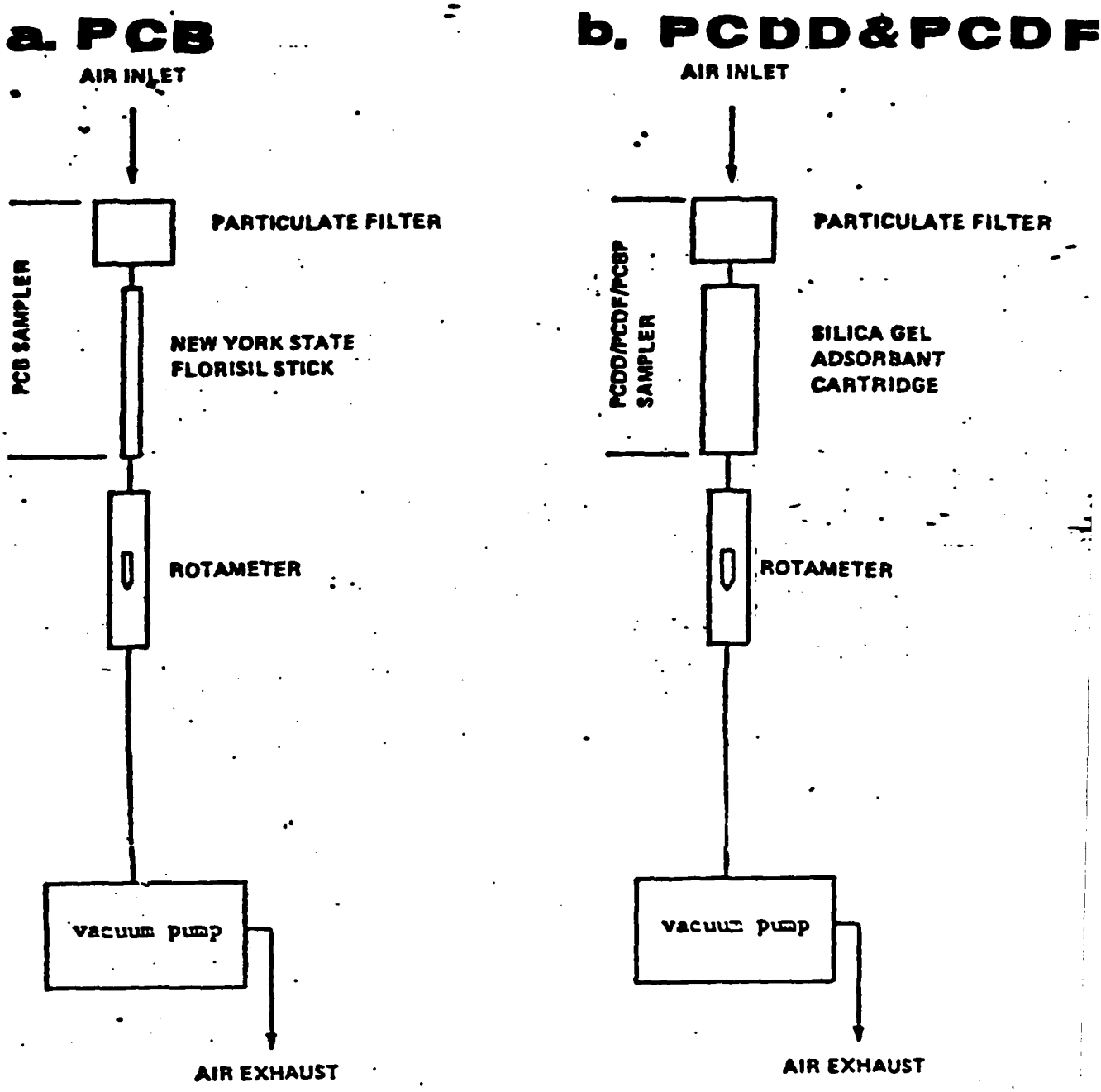

FIGURE 2. AIR SAMPLING APPARATUS FOR PCB and PCDD/PCDF

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